THE USE OF ESTER FRACTIONS IN DETERMINING THE PURITY OF FATS

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THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1922

UNIVERSITY OF ILLINOIS

May 25 1922

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Carl Becker

ENTITLED The Use of Ester Fractions in Determining the

Purity of Fats

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemical Engineering

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The writer wishes to express his appreciation to Dr. G.D.Beal for the suggestion of this method and for the helpfull guidance which made its solution possible.

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The Use of Ester Fractions in Determining The Purity of Fats.

I Introduction.

It is obvious that there is an urgent need for a short, reliable method for the detection of adulterants in fats and oils. There are thousands of manufacturing concerns that use great quantities of various fats and oils without any definite information as to their purity.

Of course, if it were known that a certain oil, say olive oil, was packed and shipped directly from the olive orchard, then it would be safe to say that the oil was pure. But there have been so many cases and types of oil and fat adulteration, that a concern using any quantity of oil ought to take avery precaution to determine its purity.

At present the methods of testing oils are by means of the Iodine Number, Saponification Number, Index of Refraction, and other similar physical and chemical constants, or by repeated fractional crystallization of the acids as a qualitative measure. They are not of much value, however, because an oil, by the use of two adulterants, can be adulterated so that it will exhibit the same balanced physical and chemical properties as the pure oil. For example, an oil like olive oil (Iodine Number 90) can be adulterated with two cheap oils, one having a higher iodine number and the other a lower iodine number than 90. By regulating the proportions in which they are added, an

iodine number of 86-90 can be obtained which is the range of iodine numbers of olive oil.

The index of refraction varies approximately as the iodine number and molecular weight, that is, it increases with the degree of unsaturation and with the number of carbon atoms in the molecule. From this it can be seen that if the iodine value of an oil is duplicated, then the index of refraction also becomes approximately equal to that of the pure oil.

The saponification numbers of practically all fats and oils are within such a close range that they offer very little evidence as to the purity of the fat, except with such very unusual fats as coconut oil and butter fat.

Thus it can be seen that the iodine number, saponification number, and index of refraction, are of no great value in determining the nature of the adulterations of a fat.

It was thought the acids of the fats used in balancing each other as adulterants of a third fat may vary among themselves in one of their constants to such an extent, that if a derivative of the entire fat may be obtained which can be fractionated, the acids of the mixture will distribute themselves among the fractions in a fashion different from the acids of the genuine fat. One of the most important steps in the examination of a volatile oil depends upon the comparison of the constants of a fractionated oil

with those of a similar series of constants from a genuine oil.

II Method.

The esters of fatty acids may be prepared from a fat by the method of Haller[1]. 500 grams of the oil are esterified with 1000 cc. of absolute methyl alcohol saturated with dry hydrochloric acid gas by refluxing for twenty hours. The whole is then poured over a salt-ice mixture and stirred vigorously. Then the ester layer is separated from the alcohol and glycerine, shaken with Barium carbonate to remove any free mineral acid, and then distilled under reduced pressure into five equal fractions. The Iodine and Saponification Numbers and the Indeces of Refraction of these fractions are then determined and compared with the constants obtained by using a similr quantity of the pure oil or fat.

Tables 3,4,5,6,7, and 8 show the constants that were obtained from samples of pure Cotton Seed Oil, Linseed Oil, and Soy Bean Oil.

Tables 9,10, 11,12,13, and 14 show the results obtained by using the adulterated samples as indicated.

Table 15 was obtained from a sample of crude Soy Bean Oil.

Tables 1 and 2 were obtained by distilling the esters at equal temperature ranges. Fractions were taken every 4°C.

Pure Cotton Seed Oil

Equal Temperature Range Fractions

Table 1. First Run

Fraction	I	II	III	IV	V
Iod. No.	80.5	96.2	120.6	136.2	123.0
Sap. No.	198.6	198.5	195.6	194.8	178.0
Index Ref.	1.4546	1.4550	1.4586	1.4629	1.4696
Pres. mm.	30.0	- -	- -	- -	- -
Temp.° C.	-218	218-22	222-26	226-30	230-35

Table 2. Second Run

Fraction	I	II	III	IV	V
Iod. No.	78.4	98.7	119.0	134.0	119.6
Sap. No.	199.8	198.0	194.2	193.2	175.9
Index Ref.	1.454	1.4559	1.4584	1.4623	1.4686
Pres. mm.	30.0	- -	- -	- -	- -
Temp.° C.	-218	218-23	223-26	226-31	231-36

Table 3. Equal Volume Fractions

First Run

Fraction	I	II	III	IV	V
Iod. No.	80.0	95,0	110.1	123.5	134.6
Sap. No.	198.9	195.6	193.5	190.2	188.6
Index Ref.	1.454	1.457	1.458	1.459	1.463
Pres. mm.	28.0	- -	- -	- -	- -
Temp.° C.	-216	216-20	220-22	222-24	224-31

Equal Volume Fractions of Cotton Seed Oil--Cont.

Table 4. Second Run

Fraction	I	II	III	IV	V
Iod. No.	81.0	95.2	111.0	122.9	133.9
Sap. No.	198.0	194.9	193.0	191.3	189.0
Index Ref.	1.4543	1.4571	1.4583	1.4594	1.4633
Pres. mm.	26.0	- -	- -	- -	- -
Temp.° C.	-216	216-20	220-22	222-23	223-30

Pure Soy Bean Oil

Equal Volume Fractions

Table 5. First Run

Fraction	I	II	III	IV	V
Iod. No.	112.0	134.0	135.0	144.5	136.3
Sap. No.	192.0	191.0	190.0	189.5	189.0
Index Ref.	1.4566	1.4585	1.4594	1.460	1.465
Pres. mm.	17.0	- -	- -	- -	- -
Temp.° C.	-210	210-13	213-14.5	214.5-17	217-25

Table 6. Second Run

Fraction	I	II	III	IV	V
Iod. No.	113.0	124.7	134.2	143.9	135.6
Sap. No.	193.0	191.6	190.6	190.0	189.0
Index. Ref.	1.4570	1.4588	1.4595	1.4596	1.4648
Pres. mm.	17.0	- -	- -	- -	- -
Temp.° C.	-211	211-12	212-13.5	213.5-18	218-24

Pure Linseed Oil

Equal Volume Fractions

Table 7. First Run

Fraction	I	II	III	IV	V
Iod. No.	166.0	178.0	185.0	192.1	191.0
Sap. No.	193.0	L83.5	181.5	178.5	173.0
Index Ref.	1.465	1.4652	1.4665	1.4667	1.4675
Pres. mm.	14.0	- -	- -	- -	- -
Temp.° C.	-209	209-10	210-11	211-12	212-14

Table 8. Second Run

Fraction	I	II	III	IV	V
Iod. No.	166.5	178.5	184.8	192.4	191.1
Sap. No.	193.6	184.0	182.0	178.0	173.8
Index Ref.	1.465	1.4653	1.466	1.4669	1.4678
Pres. mm.	14.0	- -	- -	- -	- -
Temp.° C.	-208	208-10	210-11	211-12	212-16

25% Cotton Seed Oil and 75% Linseed Oil

Table 9.

Fraction	I	II	III	IV	V
Iod. No.	142.8	157.2	164.4	177.4	178.8
Sap. No.	194.5	186.0	184.2	180.2	177.0
Index Ref.	1.4605	1.462	1.464	1.465	1.466
Pres. mm.	20.0	- -	- -	- -	- -
Temp.° C.	-215	215-16	216-17	217-18	218-24

5% Cotton Seed Oil and 95% Linseed Oil

Table 10.

Fraction	I	II	III	IV	V
Iod. No.	161.8	173.2	178.8	188.2	189.0
Sap. No.	193.9	184.5	182.9	179.0	174.6
Index Ref.	1.4627	1.4640	1.4650	1.4660	1.4670
Pres. mm.	18.0	- -	- -	- -	- -
Temp.° C.	-214	214-16	216-17	217-18	218-25

2% Cotton Seed Oil and 98% Linseed Oil

Table 11.

Fraction	I	II	III	IV	V
Iod. No.	163.0	175.2	180.9	190.3	190.6
Sap. No.	193.7	184.4	182.9	179.0	174.6
Index Ref.	1.4635	1.4647	1.4655	1.4664	1.4673
Pres. mm.	18.0	- -	- -	- -	- -
Temp.° C.	-214	214-16	216-18	218-19	219-24

5% Linseed Oil and 95% Cotton Seed Oil

Table 12.

Fraction	I	II	III	IV	V
Iod. No.	86.0	100.6	116.4	127.3	137.2
Sap. No.	196.4	193.1	192.0	190.2	189.9
Index Ref.	1.4560	1.4589	1.4596	1.4619	1.4641
Pres. mm.	16.0	- -	- -	- -	- -
Temp.° C.	-208	208-12	212-14	214-15	215-20

5% Soy Bean and 95% Cotton Seed Oil

Table 13.

Fraction	I	II	III	IV	V
Iod. No.	83.1	99.8	113.2	124.2	135.2
Sap. No.	198.0	195.2	194.0	190.2	189.9
Index Ref.	1.4548	1.4576	1.4587	1.4596	1.4638
Pres. mm.	16.0	- -	- -	- -	- -
Temp.° C.	-207	207-12	212-15	215-16	216-20

5% Cotton Seed Oil and 95% Soy Bean

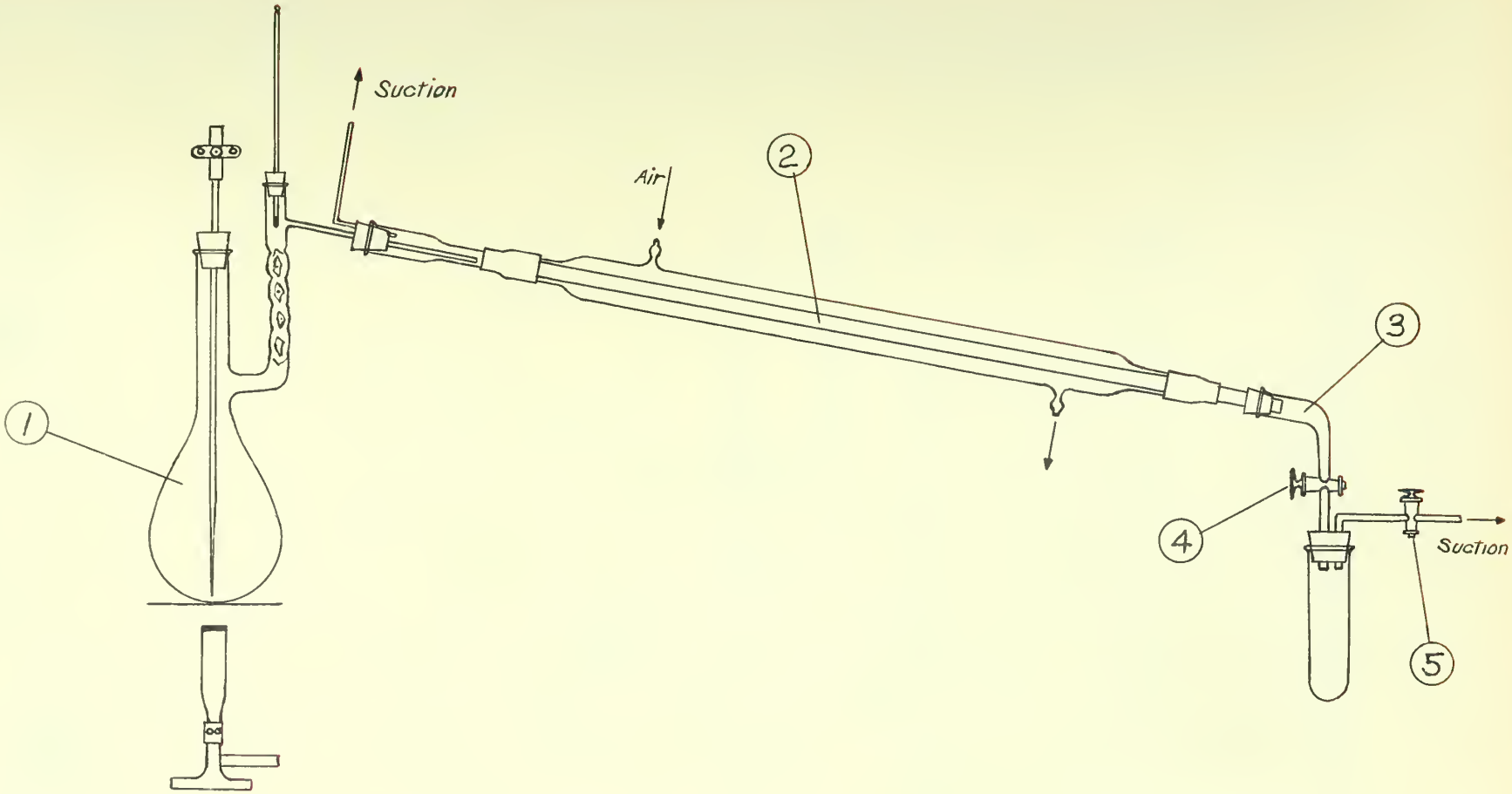
Table 14.

Fraction	I	II	III	IV	V
Iod. No.	109.6	122.1	133.2	141.9	136.0
Sap. No.	192.6	191.9	189.9	189.5	189.6
Index Ref.	1.4558	1.4580	1.4590	1.4598	1.4643
Pres. mm.	16.0	- -	- -	- -	- -
Temp.° C.	-210	210-12	212-15	215-17	217-23

Crude Soy Bean Oil

Table 15.

Fraction	I	II	III	IV	V
Iod. No.	110.3	118.9	133.9	142.7	137.9
Sap. No.	193.0	190.2	190.0	189.5	189.0
Index Ref.	1.4565	1.4582	1.4595	1.4605	1.4620
Pres. mm.	21.0	- -	- -	- -	- -
Temp.° C.	-209	209-11	211-12	212-13	213-31



— Fractional Distillation Apparatus —

Description of Apparatus in the Diagram

(1) Jena, Claissen flask with an indented side neck. 1 liter.

(2) Ordinary 90 cm. condenser tube.

(3) Adapter welded to $\frac{1}{8}$ in. stopcock.(4).

(5) Stopcock.

(6) $1\frac{1}{2}$ in. test tube.

III Apparatus and Details

Cutting the ester fractions at constant, definite temperature ranges was found difficult and inaccurate, and was abandoned for the equal volume-fraction method. The diagram show the set-up for this method.

At first, the absolute methyl alcohol was prepared by refluxing it with chemical lime (8 liters of alcohol to 1800 grams of lime) and then distilling off the alcohol. Then it was found that by using the ordinary methyl alcohol with calcium chloride, excellent results could be obtained. To 500 grams of oil and 1 liter of alcohol, saturated with hydrochloric acid gas, were added 100 grams of anhydrous calcium chloride; this was then refluxed in the usual way for fifteen or twenty hours. Sometimes at the end of this period the ester layer would fail to separate, but by adding 25-50 grams more of calcium chloride and refluxing for thirty minutes, a perfect separation was obtained.

Before distilling a batch of esters, the volume must be determined and then fractions taken so that the entire distillate will be divided into five equal parts. From 500 grams of oil the yield of esters is usually about 500 grams having a volume of about 430 cc. From this volume of esters about 21 cc. are lost in volatilization and residue as a result of the distillation. This loss is approximately proportional to the initial volume of the esters, thus making it easy to calculate the volume of the fractions to be taken for any oil.

Test tubes of ordinary glass were used to collect the fractions. They are calibrated accurately enough for this work by a pencil mark on a gummed label glued to the outside of the tube.

A pressure of 15-20 mm. of mercury was obtained by the use of an ordinary water suction pump. No difficulty was encountered with leaks. Rubber stoppers were used, protected with tin foil. If leaks occur, they can be easily stopped with a paste of glycerine and lead oxide, or with shellac.

When the distillation is ready to proceed, stopcock #4 is open and #5 closed. When the desired volume has passed over #4 is closed and #5 opened to release the vacuum. Then the test tube is removed and another put in place. Then suction is applied to #5 and when the tube is evacuated, #5 is closed and #4 opened. In this way the distillation proceeds uninterruptedly. A Raikow receiver was used at first, but this was found to be very troublesome and was replaced by the method described.

IV Solutions and Determination of Constants

Hanus Solution[2]

13.2 grams of iodine and 3 cc. of bromine were dissolved in 1 liter of glacial acetic acid, and kept in a brown, glass-stoppered bottle.

Iodine Numbers were determined as follows: 0.250 grams of the oil are weighed into a glass stoppered flask and dissolved in 10 cc. of chloroform. Then 25 cc. of Hanus solution is added. The stopper is moistened with 15% potassium iodide solution and the groove between the stopper and the edge of the flask, filled with the same solution. The solutions are allowed to stand for 2 hours in the dark and then titrated with sodium thiosulfate, after the addition of 10 cc. of a 15% solution of potassium iodide and 150 cc. of water.

The absorbtion of iodine by the unsaturated esters depends upon the mass action law, and unless a large excess of iodine is present, poor results will be obtained.

For oils with Iodine Numbers up to 135, use 25 cc. of Hanus solution for a 0.2500 gram sample; above 135, use 40 cc.

Alcohol Potash Solution

Dissolve 32 grams of potassium hydroxide in a very small amount of water and filter if necessary. Add this to 1 liter of ethyl alcohol and also $\frac{1}{2}$ gram of sodium peroxide. Shake, and allow to stand for several hours. Then filter and keep it in a glass stoppered bottle.

Saponification Numbers were determined as follows[3]: 0.2 grams of the ester are weighed into a 250 cc. flask and dissolved in 25 cc. of alcoholic potash solution. The solution is the refluxed for $\frac{1}{2}$ hour and titrated hot with $\frac{N}{2}$-hydrochloric acid, using phenolphthalein as an indicator.

Cork, and not rubber, must be used to connect the condenser and flask for the refluxing, because the alcohol dissolves some of the rubber and discolors the solution, masking the end-point.

Sodium Thiosulfate

A $\frac{N}{10}$ solution of sodium thiosulfate was made up and allowed to stand several days before indirect standardization against arsenous oxide. The solution was protected with a soda-lime tube against carbon dioxide.

This solution was used for titrating the excess Hanus solution in determining the Iodine Numbers.

Hydrochloric Acid

A $\frac{N}{2}$ solution of hydrochloric acid was made up and standardized against sodium carbonate, using methyl orange as an indicator.

Index of Refraction[4]

The indeces of refraction were determined with an Abbe Refractometer at 24°C. These values for 24° can be reduced to the usual standard of 20° by using the factor 0.00038 for each degree Centigrade, remembering that the refractive index decreases with an increase in temperature.

V Conclusions

In the writers opinion this method is reliable and can accurately detect adulteration in fats and oils as low as 5%, and in a good many cases as low as 2%.

The determination of the Saponification Numbers and Refractive Indices is not necessary. The Iodine Number is sufficient to determine whether or not the oil is pure.

The Saponification Number is not of much value, because the range of its values is so small that even a 10% adulteration would not cause an appreciable difference in the Saponification numbers of the corresponding fractions of the pure and the adulterated oil.

The Index of Refraction is also unreliable, because there seems to be other factors, besides the degree of unsaturation, and the number of carbon atoms, that effect its value.

By a study of the tables given, it can be readily seen that the Iodine Number immediately reveals any appreciable adulteration.

The degree of adulteration, of course, cannot be determined, but can be reasonably estimated.

This method should be practical, because it requires no apparatus except that which is found in any commercial laboratory. The ordinary water vacuum pump supplies sufficient suction. It is not necessary that the pressure be constant, because the fractions are cut by volume and not temperature.

VI Bibliography

(1) Compt. rend., 1906(143), 657.

(2) Zeits. f. Unters. d. Nahrgs-u. Genussm., 1901, 913.

(3) Lewkowitsch vol. 1 p.380.

(4) Lewkowitsch vol. 1 p.328.